OFFICE OF NAVAL RESEARCH

Contract Nonr-982 (03)

NR-019-135

ANNUAL SUMMARY REPORT

Period

December 1, 1954 - November 30, 1955

UNIVERSITY OF OKLAHOMA RESEARCH INSTITUTE

Norman, Oklahoma

Submitted by

K. Keith Innes

CHARACTERIZATION OF THE ALUMINUM OXIDES AND DIATOMIC ALUMINUM

Excitations of electronic spectra in the systems Al-O_2-N_2, Al-a: Al-N_2 and Al-Al_2O_3-He have been investigated at the University of Ok Naval Ordnance Laboratory and Vanderbilt University. These studies gested fruitful lines of research for complete descriptions of the spect thermochemistry of AlO, AlN and Al_2.

A. Aluminum arc in air (Al-O_2-N_2)

Since the only previous full development of emission by any of th species was by means of a four to eight ampere aluminum arc[1] the firs to extend the arc spectrum. This was most practical in the red where analogous to those already observed for molecules isoelectronic with A expected, and where atomic lines of aluminum are not plentiful and str currents of eight to ten amperes, the very unsteady flame of the arc w graphed at a dispersion of 5 Å/mm.[2] A complex band system was ob intensity of about five per cent of that of the green bands of AlO, and st 7500 Å to the infrared limit of Kodak I-M plates. Analysis of the struc not practical.

B. Aluminum-aluminum oxide arc in air (Al-alundum-N_2-O_2)

It was evident that higher dispersion photographs of the new "red were necessary if analysis was to be effected. This would require long

---

1 Pearse and Gaydon, "Identification of Molecular Spectra" 2nd e p. 51 and Plate I, the well known "green bands" of AlO, $\lambda\lambda$ 4400-5400.

2 Three-meter grating spectrograph of the U. S. Naval Ordnanc Laboratory, White Oak, Maryland.

CHARACTERIZATION OF THE ALUMINUM OXIDES AND OF

DIATOMIC ALUMINUM

Excitations of electronic spectra in the systems $Al-O_2-N_2$, Al-alundum-O_2-N_2, $Al-N_2$ and $Al-Al_2O_3-He$ have been investigated at the University of Oklahoma, the Naval Ordnance Laboratory and Vanderbilt University. These studies have suggested fruitful lines of research for complete descriptions of the spectra and thermochemistry of AlO, AlN and Al_2.

A. Aluminum arc in air ($Al-O_2-N_2$)

Since the only previous full development of emission by any of the desired species was by means of a four to eight ampere aluminum arc[1] the first attempt was to extend the arc spectrum. This was most practical in the red where a band system analogous to those already observed for molecules isoelectronic with AlO was expected, and where atomic lines of aluminum are not plentiful and strong. Using currents of eight to ten amperes, the very unsteady flame of the arc was photographed at a dispersion of 5 Å/mm.[2] A complex band system was observed, with intensity of about five per cent of that of the green bands of AlO, and strongest from 7500 Å to the infrared limit of Kodak I-M plates. Analysis of the structure was not practical.

B. Aluminum-aluminum oxide arc in air (Al-alundum-N_2-O_2)

It was evident that higher dispersion photographs of the new "red bands" were necessary if analysis was to be effected. This would require longer exposures

1 Pearse and Gaydon, "Identification of Molecular Spectra" 2nd ed., p. 51 and Plate I, the well known "green bands" of AlO, $\lambda\lambda$ 4400-5400.

2 Three-meter grating spectrograph of the U. S. Naval Ordnance Laboratory, White Oak, Maryland.

(ca. 45 minutes) and, therefore, a steadier arc. The latter was achieved by packing the aluminum electrode tips in alundum cement and by carrying the heat of the arc away by water-cooling the aluminum rods. It was hoped that the TiO_2 and ZrO_2 in the alundum cement would not give enough TiO and ZrO to mask the desired "red bands." For example, Phillips[1] found that observation of red bands of TiO using a 21-foot grating required exposure of a high tension arc for 20 minutes at 6600 Å, and 60 minutes at 8000 Å.

A seven to eight ampere arc between the modified electrodes was exposed for 40 minutes at a dispersion of 1.25 Å /mm.[2] The band structure was very complex over the region 6500-9000 Å. Lines were so close together that branches could be picked out only after the wave number measurement of the more than 20000 lines. Even then the lines were so badly superimposed that it was difficult to find branches with reasonable intensity distributions. Thus the only outstanding features were regularly spaced lines at 7340 and 7160 Å on an otherwise clean background. These features indicate a B-value of about 0.2 cm^{-1}, as would be expected for Al_2. However, no intensity alternation was observed and, in the absence of Q-branches, the analysis could not be carried further. It is likely that other tentative bands (of quite different spacing) could be confirmed if the spectrum could be simplified and/or photographed at still higher resolution. The higher resolution could be obtained only in "cooler" sources which would give narrower spectral lines, as discussed in D and E. Lower effective temperatures will also

---

1 J. G. Phillips, Astrophys. J. 114, 152 (1951).

2 Twenty-one foot grating spectrograph at Johns Hopkins University.

simplify the spectrum by involving fewer vibrational states. But it is evident from analysis to date that several emitters are responsible for the spectrum, and the greatest simplification should be achieved by viewing them one at a time, as discussed particularly in C.

C. Aluminum arc in nitrogen ($Al-N_2$)

To test our impression that more than one emitter contribute to the new red bands of the aluminum arc, a closed arc was designed wherein pure Al tips fit into water-cooled Al holders, which, in turn, slide through O-ring seals into a closed cylinder of brass. This arc was burned at about eight amperes in air and in N_2, each at one atmosphere, and the emission was photographed at a dispersion of 5 Å/mm. Atomic aluminum lines are observed much more strongly in the flame in a nitrogen atmosphere--where the band structure is selectively weaker--than from the flame in air. Particularly at lower wavelengths, bands which clearly persist in nitrogen can presumably be assigned to AlN. For the desirable study of the AlN bands at higher dispersion, the arc holder needs to be redesigned so that longer burnings are possible. This is also desirable for the study of the arc burning in $He-O_2$ mixtures, where heat dissipation is a much greater problem. Modified designs for closed arcs are being considered.

D. Stainless steel hollow cathode containing $Al-Al_2O_3$ ($Al-Al_2O_3-He$)

We operated a hollow-cathode discharge tube of conventional design (pyrex envelope) at currents of 25-500 ma. in an attempt to observe, for the first time in a discharge tube, the green bands of AlO. The green bands developed at 450-500 ma. and were very intense. Extensive study of the green bands at the higher resolution made possible by this "low" temperature source, and investigation of accompanying emission in other regions (red bands ?) at correspondingly high resolution, seems very desirable; in fact, may be termed the most promising hope for further study of AlO. The major defect in the discharge tubes first used was that the thin-walled cathodes employed could not withstand attack by hot aluminum for an appreciable length of time. It is felt that a heavier cathode, or perhaps one made of tungsten, will contain the aluminum for, say, thirty minutes. Such a cathode will be tried.

E. King furnace

A second method of reducing the temperature of observation is being explored during summers at the Naval Ordnance Laboratory. A high temperature electric furnace, suitable for absorption or emission spectroscopy,[1] has now been completed by the shop there. The green bands of AlO have already been observed in emission as an impurity in such a furnace[1] and it is hoped that with charges of Al-Al_2O_3 in an inert atmosphere the spectrum of AlO may be explored rather completely.

1 P. B. Zeeman, Can. J. Phys. 32, 9 (1954).

OFFICE OF NAVAL RESEARCH
PHYSICS BRANCH
TECHNICAL REPORTS DISTRIBUTION LIST
for

A. Government Distribution

1. Department of Defense

Asst. Sec. of Defense for Research and Development
Information Office Library Branch
Pentagon Building
Washington 25, D. C. (2 copies)

Armed Services Technical Information Agency
Documents Service Center
Knott Building
Dayton 2, Ohio (5 copies)

2. Department of the Navy

Chief, Bureau of Aeronautics
TD-4
Navy Department
Washington 25, D. C.

Chief, Bureau of Ordnance
Rea
Navy Department
Washington 25, D. C.

Chief, Bureau of Ships
Code 300
Navy Department
Washington 25, D. C.

Chief of Naval Research
Office of Naval Research
Washington 25, D. C.
Attn: Physics Branch (Code 421)(3 copies)

Director
Naval Research Laboratory
Technical Information Officer (Code 2000) (6 copies)
Code 2021 (2 copies)
Washington 25, D. C.

Commanding Officer
Office of Naval Research Branch Office
150 Causeway Street
Boston 14, Massachusetts (Boston area only)

Commanding Officer
Office of Naval Research Branch Office
346 Broadway
New York 13, New York

Contract Administrator
Southeastern Area
Office of Naval Research
George Washington University
2110 G. Street, N. W.
Washington 7, D. C.

Commanding Officer
Office of Naval Research Branch Office
86 East Randolph Street
Chicago 1, Illinois

Commanding Officer
Office of Naval Research Branch Office
1030 East Green Street
Pasadena 1, California

Commanding Officer
Office of Naval Research London Branch Office
Navy #100
Fleet Post Office
New York, New York (2 copies)

Librarian
U. S. Naval Post Graduate School
Monterey, California

U. S. Naval Electronics Laboratory Library
San Diego 52, California

Commanding Officer
U. S. Naval War College
Newport, Rhode Island

Director
Research Department
Naval Ordnance Laboratory
White Oaks, Maryland

Commanding Officer
Physics Division
Naval Ordnance Test Station
Inyokern
China Lake, California

Commanding Officer
U. S. Naval Ordnance Laboratory
Corona, California

3. Department of the Air Force

Commanding General
Wright Air Development Center
Wright-Patterson Air Force Base
Dayton, Ohio

Commanding General
Air Research and Development Command
Attn: Office of Scientific Research
Post Office Box 1395
Baltimore 3, Maryland (2 copies)

Commander
Air Force Cambridge Research Center
230 Albany Street
Cambridge, Massachusetts
Attn: CRHCP-1

4. Department of the Army

Commanding Officer
Engineering Research and Development Laboratories
Fort Belvoir, Virginia
Attn: Technical Intelligence Branch

Office of Ordnance Research
Box CM, Duke Station
Durham, North Carolina (2 copies)

Signal Corps Engineering Laboratory
Fort Monmouth, New Jersey
Attn: Technical Information Officer

Dr. J. L. Martin
Watertown Arsenal
Watertown 72, Massachusetts

5. Department of Commerce

Office of Technical Services
Technical Reports Section
Department of Commerce
Washington 25, D. C.

Director
National Bureau of Standards
Washington 25, D. C.

6. Other Agencies

National Research Council
Division of Physical Sciences
National Academy of Sciences
Washington 25, D. C.

Director
National Science Foundation
Washington 25, D. C.

U. S. Atomic Energy Commission
Technical Information Service
P. O. Box 62
Oak Ridge, Tennessee

Atomic Energy Commission
Washington 25, D. C.

Dr. D. Bleil
Naval Ordnance Laboratory
White Oak, Silver Spring, Maryland

Dr. E. H. Winkler
Naval Ordnance Laboratory
White Oak, Silver Spring, Maryland

Dr. L. Morris
Naval Ordnance Laboratory
White Oak, Silver Spring, Maryland

Dr. Willard H. Bennett
Naval Research Laboratory
Washington 25, D. C.

ELECTRONIC STRUCTURE OF MOLECULES
Non-Government List

Professor R. S. Mulliken
Department of Physics
University of Chicago
Chicago, Illinois

Dr. D. F. Hornig
Brown University
Providence, Rhode Island

Prof. J. R. Holmes
University of Southern California
Los Angeles, California

Prof. K. W. Meissner
Purdue University
Lafayette, Indiana

Dr. R. B. King
Physics Department
California Institute of Technology
Pasadena, California

Professor W. W. Beeman
University of Wisconsin
Madison, Wisconsin

Prof. D. S. McClure
Chemistry Department
University of California
Berkeley 4, California

Prof. M. Kasha
Department of Chemistry
Florida State University
Tallahassee, Florida

Dr. K. K. Innes
Department of Chemistry
University of Oklahoma
Norman, Oklahoma